

PATENT SPECIFICATION

(11) 1 323 710

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NO DRAWINGS

- (21) Application No. 48094/70 (22) Filed 9 Oct. 1970
 (31) Convention Application No. 865 470 (32) Filed 10-Oct. 1969 in
 (33) United States of America (US)
 (44) Complete Specification published 18 July 1973
 (51) International Classification: C10G 29/02, 23/02
 (52) Index at acceptance
 C5E 1: 20 21E
 C1A D41 DX G12 G12D41 G12DX G3 G4 G42 G47
 G50 G55
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(54) SHAPE SELECTIVE CONVERSION PROCESS FOR DEWAXING HYDROCARBON MIXTURES

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to dewaxing processes carried out in the presence of crystalline zeolitic material and, more particularly, to the removal of straight-chain paraffins and slightly branched-chain paraffins from hydrocarbon feedstocks by selectively converting these materials from a mixture of the same with the other components generally found in hydrocarbon feedstocks.

Hydrocarbon conversion processes utilizing crystalline zeolites and, in particular, aluminosilicate catalysts have been the subject of extensive investigation during recent years as is obvious from both the patent and scientific literature. Crystalline aluminosilicates have been found to be particularly effective for a wide variety of hydrocarbon conversion processes and have been described and claimed in many patents including United States Patent 3,140,249; 3,140,252; 3,140,251; 3,140,253; and 3,271,418. Aside from serving as general catalysts in hydrocarbon conversion processes, it is also known that the molecular sieve properties of zeolites can be utilized to preferentially convert one molecular species from a mixture of the same with other species.

In a process of this type a zeolitic molecular sieve is employed having catalytic activity within its internal pore structure and pore openings such that one component of a feed is capable of entering within the internal pore structure thereof and being converted to the substantial exclusion of another component

which, because of its size, is incapable of entering within the pores of the zeolitic material. Shape selective catalytic conversion is also known in the art and is disclosed and claimed in: United States Patent 3,140,322; 3,379,640 and 3,395,094.

Although a wide variety of zeolitic materials and particularly crystalline aluminosilicates have been successfully employed in various catalytic conversion processes, nevertheless, these prior art processes, in general, fell into one or two main categories. In one type of conversion process a zeolite was employed which had a pore size sufficiently large to admit the vast majority of components normally found in a charge, i.e., these materials are referred to as large pore size molecular sieves and they are generally stated to have a pore size of from 6 to 13 Angstroms and are represented by zeolites X, Y and L. The other type of aluminosilicate was one which had a pore size of approximately 5 Angstrom units and it was utilized to preferentially act upon normal paraffins to the substantial exclusion of other molecular species. Thus, by way of considerable over-simplification up until the present invention, there were only two types of aluminosilicates which were available for hydrocarbon processing—those which would admit only normal paraffins and those which would admit all components normally present in a hydrocarbon feed charge.

It has now been discovered that very effective catalytic operations can be carried out by utilizing a class of zeolitic molecular sieves which possess unique sieving properties in that they allow entry and egress to their internal pore structure of not only normal paraffins but also of slightly branched paraffins, and yet have the ability to exclude heavily branched isoparaffins. Thus, it is now possible to carry out hydrocarbon conversion processes which are not only selective towards normal paraffins,

but also are selective towards slightly branched paraffins and, in particular, monomethyl-substituted paraffins. It has now been discovered that when zeolitic materials exhibiting these properties are employed in those dewaxing operations where it has been heretofore desirous only to selectively remove normal paraffins that many increased and unexpected benefits will occur in that the resulting products have enhanced economic value.

As has heretofore been stated, all the crystalline aluminosilicate materials heretofore employed in prior art processes fell into one of two general types. They either have pore sizes of about 5 Angstrom units or have pore sizes from about 6 to about 15 Angstrom units. The 5 Angstrom unit aluminosilicates were generally stated to be shape selective in that they allowed selective conversion of normal aliphatic compounds from a mixture of the same with isoaliphatic compounds and cyclic compounds. The second type of aluminosilicate, i.e., those having a pore size of 6 to 15 Angstrom units were generally stated to be nonselective, i.e., substantially all of the molecules normally found in a hydrocarbon feed stream are able to enter within the internal pore structure of the zeolites and be converted. Thus, heretofore a very convenient method of identifying a good shape selective catalyst was to show that it would selectively crack normal hexane from a mixture of the same with 2-methyl pentane since the former was able to enter its internal pore structure, whereas the latter isocompound was unable to do so.

The dewaxing process of this invention is predicated upon using zeolite materials which can generally be stated to be intermediate between the two types of aluminosilicates heretofore employed. Thus, catalysts employed in this invention will allow the entry into their internal pore structure of normal aliphatic compounds and slightly branched aliphatic compounds, particularly monomethyl-substituted compounds, yet substantially exclude all compounds containing at least a quaternary carbon atom or having a molecular dimension equal to or substantially greater than a quaternary carbon atom. Additionally, aromatic compounds having side chains similar to the normal aliphatic compounds and slightly branched aliphatic compounds above described could have said side chains enter the internal pore structure of the instant catalysts. Thus, if one were to measure the selectivity of the zeolitic materials employed in the processes of this invention by the heretofore mentioned prior art test, i.e., the ability to selectively crack hexane from a mixture of the same with isohexane, these catalysts would have to be stated as being non-shape selective. It should be immediately apparent, however, that the term selectivity has a far greater significance than merely the ability to preferentially distinguish between normal paraffins and isoparaffins. Selectivity

on shape is theoretically possible at any shape or size although, quite obviously, such selectivity might not result in an advantageous catalyst for any and all hydrocarbon conversion processes.

The dewaxing processes of this invention are based upon the fact that, although it is art-recognized that in the vast majority of refinery operations it is desirous to preserve aromatics and to remove normal paraffins, nevertheless, such a generalization is not the final word in obtaining maximum yields of economically enhanced products. It has now been discovered that enhanced benefits can be obtained if a catalyst system could be designed which would not only selectively convert normal paraffins but certain isoparaffins, and yet not affect desirable components in a given feedstock. This type of molecular processing or sieving was heretofore unknown. As has been stated, all the previous catalytic processing involving the use of zeolitic molecular sieves merely gave the operator two choices. He could either use a molecular sieve which was a catalyst of generalized competence, i.e., it would act upon substantially all of the molecules normally found in a hydrocarbon feed or he could use a catalyst which had a pore size of about 5 Angstrom units thereby allowing selective conversion of normal aliphatic compounds only.

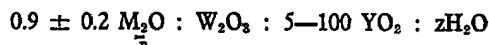
While not wishing to be bound by any theory of operation, nevertheless, the crystalline zeolitic materials employed in the present invention cannot simply be characterized by the recitation of a pore size or a range of pore sizes. The uniform pore openings of the type of zeolite employed in the invention are not circular in nature, as is usually the case in the previously employed zeolites, but rather, are elliptical in nature. Thus, the pore openings of the zeolite materials employed in the invention have both a major and a minor axes, and it is for this reason that the unusual and novel molecular sieving effects are achieved. This elliptical shape can be referred to as a "keyhole". The minor axis of the elliptical pores in the zeolites used in the invention have an effective size of about 5 Angstrom units and the major axis is from about 6 to about 9 Angstrom units. The unique keyhole molecular sieving action of these materials is presumably due to the presence of these elliptically shaped windows controlling access to the internal crystalline pore structure. It is impossible to give totally precise dimensions for the size of the pore openings in the zeolites used in the invention, and therefore some slight deviation from the above recited limits of pore opening size is permissible, and indeed contemplated, provided that the size remains such as to admit only normal and slightly branched chain hydrocarbons. It is for this reason that the limits quoted are prefaced with "about".

A test method has been devised in order to determine whether or not a zeolite possesses

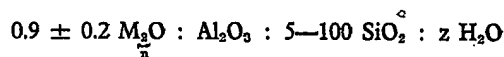
the unique molecular sieving properties necessary to carry out the novel conversion process of this invention. In said test method a candidate zeolite free from any matrix or binder is initially converted to the so-called acid or hydrogen form. This procedure involves exhaustive exchange with an ammonium chloride solution in order to replace any metallic cations originally present. The sample is then sized to 20—30 mesh and calcined in air for 16 hours at 550°C. One gram of the so-treated zeolite is then contacted with benzene at a pressure of twelve torr at a temperature of 25°C for a time period of two hours. Another gram sample is contacted with mesitylene at a pressure of 0.5 torr at a temperature of 25°C for a period of six hours. Every zeolite which has been found operable in the present invention has been one whose acid form will adsorb at least 3.0 weight percent benzene and less than 1.5 weight percent mesitylene at the above recited conditions.

Examples of zeolite materials which are operable in the process of this invention are ZSM—5 and ZSM—8 type zeolites. ZSM—5 type materials are disclosed and claimed in British Specification No. 1,161,974 and ZSM—8 is disclosed and claimed in copending Application No. 43,164/70.

The family of ZSM—5 compositions has the characteristic X-ray diffraction pattern set forth in Table 1, hereinbelow. ZSM—5 compositions can also be identified, in terms of mole ratios of oxides, as follows:



wherein M is a cation, n is the valence of said cation, W is selected from aluminum and gallium, Y is selected from silicon and germanium, and Z is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:



and M is a mixture of at least one alkali metal cation, especially sodium, with at least one tetraalkylammonium cation, the alkyl groups of which preferably contain 2—5 carbon atoms.

In a preferred embodiment of ZSM—5, W is aluminum, Y is silicon and the silica/alumina mole ratio is at least 10 and ranges up to about 60.

Members of the family of ZSM—5 zeolites possess a definite distinguishing crystalline structure whose X-ray diffraction pattern shows the following significant lines:

TABLE I

Interplanar Spacing d(A)	Relative Intensity
11.1 \pm 0.2	S
10.0 \pm 0.2	S
7.4 \pm 0.15	W
7.1 \pm 0.15	W
6.3 \pm 0.1	W
6.04 \pm 0.1	W
5.97 \pm 0.1	W
5.56 \pm 0.1	W
5.01 \pm 0.1	W
4.60 \pm 0.08	W
4.25 \pm 0.08	W
3.85 \pm 0.07	VS
3.71 \pm 0.05	S
3.64 \pm 0.05	M
3.04 \pm 0.03	W
2.99 \pm 0.02	W
2.94 \pm 0.02	W

5 These values as well as all other X-ray data were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights, I , and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From 10 these, the relative intensities, $100 I/I_0$, where I_0 is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table I the relative intensities are 15 given in terms of the symbols S=strong, M=medium, MS=medium strong, MW=medium

weak and VS=very strong. It should be understood that this X-ray diffraction pattern is characteristic of all the species of ZSM-5 compositions. Ion exchange of the sodium ion 20 with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending 25 on the silicon to aluminum ratio of the particular sample, as well as if it has been subjected to thermal treatment. Various cation exchanged forms of ZSM-5 have been prepared. X-ray powder diffraction patterns of several of these forms are set forth below. The ZSM-5 forms 30 set forth below are all aluminosilicates.

TABLE 2
X-Ray Diffraction
ZSM-5 Powder in Cation Exchanged Forms
d Spacings Observed

As made	HCl	NaCl	CaCl ₂	ReCl ₃	AgNO ₃
11.15	11.16	11.19	11.19	11.19	11.19
10.01	10.03	10.05	10.01	10.06	10.01
9.74	9.78	9.80	9.74	9.79	9.77
—	—	9.01	9.02	—	8.99
8.06	—	—	—	—	—
7.44	7.46	7.46	7.46	7.40	4.46
7.08	7.07	7.09	7.11	—	7.09
6.70	6.72	6.73	6.70	6.73	6.73
6.36	6.38	6.38	6.37	6.39	6.37
5.99	6.00	6.01	5.99	6.02	6.01
5.70	5.71	5.73	5.70	5.72	5.72
5.56	5.58	5.58	5.57	5.59	5.58
5.37	—	5.38	5.37	5.38	5.37
5.13	5.11	5.14	5.12	5.14	—
4.99	5.01	5.01	5.01	5.01	5.01
—	—	4.74	—	—	—
4.61	4.62	4.62	4.61	4.63	4.62
—	—	4.46	4.46	—	4.46
4.36	4.37	4.37	4.36	4.37	4.37
4.26	4.27	4.27	4.26	4.27	4.27
4.08	—	4.09	4.09	4.09	4.09
4.00	4.01	4.01	4.00	4.01	4.01
3.84	3.85	3.85	3.85	3.86	3.86
3.82	3.82	3.82	3.82	3.83	3.82
3.75	3.75	3.75	3.76	3.76	3.75
3.72	3.72	3.72	3.72	3.72	3.72
3.64	3.65	3.65	3.65	3.65	3.65
—	3.60	3.60	3.60	3.61	3.60

TABLE 2 (Continued)

As Made	HCl	NaCl	CaCl ₂	ReCl ₃	AgNO ₃
3.48	3.49	3.49	3.48	3.49	3.49
3.44	3.45	3.45	3.44	3.45	3.45
3.34	3.35	3.36	3.35	3.35	3.35
3.31	3.31	3.32	3.31	3.32	3.32
3.25	3.25	3.26	3.25	3.25	3.26
3.17	—	—	3.17	3.18	—
3.13	3.14	3.14	3.14	3.15	3.14
3.05	3.05	3.05	3.04	3.06	3.05
2.98	2.98	2.99	2.98	2.99	2.99
—	—	—	—	2.97	—
—	2.95	2.95	2.94	2.95	2.95
2.86	2.87	2.87	2.87	2.87	2.87
2.80	—	—	—	—	—
2.78	—	—	2.78	—	2.78
2.73	2.74	2.74	2.73	2.74	2.74
2.67	—	—	2.68	—	—
2.66	—	—	2.65	—	—
2.60	2.61	2.61	2.61	2.61	2.61
—	2.59	—	2.59	—	—
2.57	—	2.57	2.56	—	2.57
2.50	2.52	2.52	2.52	2.52	—
2.49	2.49	2.49	2.49	2.49	2.49
—	—	—	2.45	—	—
2.41	2.42	2.42	2.42	2.42	—
2.39	2.40	2.40	2.39	2.40	2.40
—	—	—	2.38	2.35	2.38
—	2.33	—	2.33	2.32	2.33
—	2.30	—	—	—	—
—	2.24	2.23	2.23	—	—

TABLE 2 (Continued)

As Made	HCl	NaCl	CaCl ₂	ReCl ₃	AgNO ₃
—	2.20	2.21	2.20	2.20	—
—	2.18	2.18	—	—	—
—	—	2.17	2.17	—	—
—	2.13	—	2.13	—	—
—	2.11	2.11	—	2.11	—
—	—	—	2.10	2.10	—
—	2.08	2.08	—	2.08	2.08
—	—	2.07	2.07	—	—
—	—	—	2.04	—	—
2.01	2.01	2.01	2.01	2.01	2.01
1.99	2.00	1.99	1.99	1.99	1.99
—	—	—	1.97	1.96	—
1.95	1.95	1.95	1.95	1.95	—
—	—	—	—	1.94	—
—	1.92	1.92	1.92	1.92	1.92
1.91	—	—	—	1.91	—
—	—	—	—	1.88	—
1.87	1.87	1.87	1.87	1.87	1.87
—	1.86	—	—	—	—
1.84	1.84	—	—	1.84	1.84
1.83	1.83	1.83	1.83	1.83	—
1.82	—	1.81	—	1.82	—
1.77	1.77	1.79	1.78	—	1.77
1.76	1.76	1.76	1.76	1.76	1.76
—	—	1.75	—	—	1.75
—	1.74	1.74	1.73	—	—
1.71	1.72	1.72	1.71	—	1.70
1.67	1.67	1.67	—	1.67	1.67
1.66	1.66	—	1.66	1.66	1.66
—	—	1.65	1.65	—	—

TABLE 2 (Continued)

As Made	HCl	NaCl	CaCl ₂	ReCl ₃	AgNO ₃
—	—	1.64	1.64	—	—
—	1.63	1.63	1.63	1.63	1.62
—	1.61	1.61	1.61	—	1.61
1.58	—	—	—	—	—
—	1.57	1.57	—	1.57	1.57
—	—	1.56	1.56	1.56	—

Zeolite ZSM—5 can be suitably prepared by preparing a solution containing tetrapropyl ammonium hydroxide, sodium oxide, an oxide of aluminum or gallium, an oxide of silica or

germanium, and water and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

TABLE 3

	Broad	Preferred	Particularly Preferred
OH ⁻ /SiO	0.07—1.0	0.1—0.8	0.1—0.75
R ₄ N ⁺ /(R ₄ N ⁺ +Na ⁺)	0.2—0.95	0.3—0.9	0.4—0.9
H ₂ O/OH ⁻	10—300	10—300	10—300
YO ₂ /W ₂ O ₃	5—100	10—60	10—40

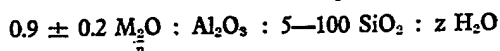
wherein R is propyl, W is aluminum or gallium and Y is silicon or germanium maintaining the mixture until crystals of the zeolite are formed. Thereafter, the crystals are separated from the liquid and recovered. Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 150°C to 175°C for a period of time of from about six hours to 60 days. A more preferred temperature range is from about 160 to 175°C with the amount of time at a temperature in such range being from about 12 hours to 8 days.

The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering and water washing.

The foregoing product is dried, e.g., at 230°F, for from about 8 to 24 hours. Of course, milder conditions may be employed if desired, e.g., room temperature under vacuum.

ZSM—5 is preferably formed as an

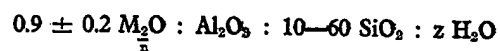
aluminosilicate. The composition can be prepared utilizing materials which supply the appropriate oxide. Such compositions include for an aluminosilicate, sodium aluminate, alumina, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide and tetrapropylammonium hydroxide. It will be understood that each oxide component utilized in the reaction mixture for preparing a member of the ZSM—5 family can be supplied by one or more initial reactants and they can be mixed together in any order. For example, sodium oxide can be supplied by an aqueous solution of sodium hydroxide, or by an aqueous solution of sodium silicate; tetrapropylammonium cation can be supplied by the bromide salt. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time of the ZSM—5 composition will vary with the nature of the reaction mixture employed. ZSM—8 can also be identified, in terms of mole ratios of oxides, as follows:



wherein M is at least one cation, n is the valence thereof and z is from 0 to 40. In a preferred synthesized form, the zeolite has a

formula, in terms of mole ratios of oxides, as follows:

5



and M is a mixture of at least one alkali metal cation, especially sodium, with tetraethylammonium cations.

ZSM-8 possesses a definite distinguishing crystalline structure having the following x-ray diffraction pattern:

10

TABLE 4

dA°	I/I ₀	I/I ₀	dA°
11.1	46	4	2.97
10.0	42	3	2.94
9.7	10	2	2.86
9.0	6	1	2.78
7.42	10	4	2.73
7.06	7	1	2.68
6.69	5	3	2.61
6.35	12	1	2.57
6.04	6	1	2.55
5.97	12	1	2.51
5.69	9	6	2.49
5.56	13	1	2.45
5.36	3	2	2.47
5.12	4	3	2.39
5.01	7	1	2.35
4.60	7	1	2.32
4.45	3	1	2.28
4.35	7	1	2.23
4.25	18	1	2.20
4.07	20	1	2.17
4.00	10	1	2.12
3.85	100	1	2.11
3.82	57	1	2.08
3.75	25	1	2.06
3.71	30	6	2.01

TABLE 4 (Continued)

dA°	I/I ₀	I/I ₀	dA°
3.64	26	6	1.99
3.59	2	2	1.95
3.47	6	2	1.91
3.43	9	3	1.87
3.39	5	1	1.84
3.34	18	2	1.82
3.31	8		
3.24	4		
3.13	3		
3.04	10		
2.99	6		

5 Zeolite ZSM—8 can be suitably prepared by reacting a solution containing either tetraethylammonium hydroxide or tetraethylammonium bromide together with sodium oxide, aluminum oxide, and an oxide of silica and water.

10 The relative operable proportions of the various ingredients have not been fully determined and it is to be immediately understood that not any and all proportions of reactants will operate to produce the desired zeolite. In fact, completely different zeolites can be pre-

pared utilizing the same starting materials depending upon their relative concentration and reaction conditions as is set forth in United States 3,308,069. In general, however, it has been found that when tetraethylammonium hydroxide is employed, ZSM—8 can be prepared from said hydroxide, sodium oxide, aluminum oxide, silica and water by reacting said materials in such proportions that the forming solution has a composition in terms of mole ratios of oxides falling within the following range

$\text{SiO}_2/\text{Al}_2\text{O}_3$ — from about 10 to about 200

$\text{Na}_2\text{O}/\text{tetraethylammonium hydroxide}$ — from about 0.05 to 0.20

$\text{Tetraethylammonium hydroxide}/\text{SiO}_2$ — from about 0.08 to 1.0

$\text{H}_2\text{O}/\text{tetraethylammonium hydroxide}$ — from about 80 to about 200

30 Thereafter, the crystals are separated from the liquid and recovered. Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 100°C to 175°C for a period of time of from about six hours to 60 days. A more preferred temperature range is from about 150 to 175°C with the amount of time at a temperature in such range being from about 12 hours to 8 days.

35 The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering, and water washing.

45 The foregoing product is dried, e.g., at 230°F, for from about 8 to 24 hours. Of course, milder conditions may be employed if desired, e.g., room temperature under vacuum.

50 ZSM—8 is prepared utilizing materials which supply the appropriate oxide. Such compositions include sodium aluminate, alumina, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide and tetraethylammonium hydroxide. It will be understood that each oxide component utilized in the reaction mixture can be supplied by one or more initial reactants and they can be mixed together in any order. For example, sodium oxide can be supplied by an aqueous solution of sodium

hydroxide, or by an aqueous solution of sodium silicate, tetraethylammonium cation can be supplied by the bromide salt. The reaction mixture can be prepared either batchwise or

continuously.
The zeolites used in the present invention can have the original cations associated therewith replaced by a wide variety of other cations according to techniques well known in the art. Typical replacing cations would include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing metallic cations, particular preference is given to cations of metals such as rare earth metals, manganese, calcium, as well as metals of Group II of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., nickel.

Typical ion exchange techniques would be to contact the particular zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion exchange techniques are disclosed in a wide variety of patents including United States 3,140,249; United States 3,140,251; and United States 3,140,253.

Following contact with the salt solution of the desired replacing cation, the zeolites are then preferably washed with water and dried at a temperature ranging from 150°F to about 600°F and thereafter calcined in air or other inert gas at temperatures ranging from about 500°F to 1500°F for periods of time ranging from 1 to 48 hours or more. It has been further found in accordance with the invention that catalysts of improved selectivity and having other beneficial properties in some hydrocarbon conversion processes such as catalytic cracking are obtained by subjecting the zeolite to treatment with steam at elevated temperatures ranging from 800°F to 1500°F and preferably 1000°F and 1400°F. The treatment may be accomplished in an atmosphere of 100% steam or in an atmosphere consisting of steam and a gas which is substantially inert to the zeolites.

A similar treatment can be accomplished at lower temperatures and elevated pressures, e.g., 350–700°F at 10 to about 200 atmospheres. The zeolites can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation/dehydrogenation function is to be performed, i.e., shape selective hydrocracking. Such component can be exchanged into the composition, impregnated therein or physically intimately admixed therewith. Such component can be impregnated in or onto zeolite such as, for example, by, in the case of platinum, treating the zeolite with a platinum metal-containing

ion. Thus, suitable platinum compounds include chloroplatinic acid, platinum chloride and various compounds containing a platinum ammine complex.

The compounds of the useful platinum or other metals can be divided into compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds which contain the metal in the ionic state can be used. A solution in which platinum metals are in the form of a cation or cationic complex, e.g., $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is particularly useful.

Prior to use, the zeolites should be dehydrated at least partially. This can be done by heating to a temperature in the range of 200 to 600°C in an inert atmosphere, such as air or nitrogen, and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at lower temperatures merely by using a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

As has heretofore been pointed out, the process of this invention is concerned with dewaxing of hydrocarbon feedstocks. The term "dewaxing" as used in the specification and claims is used in its broadest sense and is intended to mean the removal of those hydrocarbons which readily solidify (waxes) from petroleum stocks. As will be further illustrated in the specific examples, hydrocarbon feeds which can be treated include lubricating oil stocks as well as those which have a freeze point or pour point problem, i.e., petroleum stocks boiling above about 350°F. The dewaxing can be carried out at either cracking or hydrocracking conditions.

Typical cracking conditions include a liquid hourly space velocity between about 0.5 and 200, a temperature between about 550°F and 1100°F, a pressure between about subatmospheric and several hundred atmospheres.

When hydrocracking operations are carried out, operating conditions include temperatures between 650°F and 1000°F, a pressure between 100 and 3000 psig but preferably between 200 and 700 psig. The liquid hourly space velocity is generally between 0.1 and 10, preferably between 0.5 and 4 and the hydrogen to hydrocarbon mole ratio is generally between 1 and 20 preferably between 4 and 12.

The following examples will illustrate the best mode now contemplated for carrying out this invention.

EXAMPLE 1

This example will illustrate a typical preparation of zeolite ZSM-5. 22.9 grams SiO_2 was partially dissolved in 100 ml 2.18N tetrapropylammonium hydroxide by heating to a temperature of about 100°C. There was then added a mixture of 3.19 grams NaAlO_2 (comp: 42.0 wt. % Al_2O_3 , 30.9% Na_2O ,

- 27.1% H₂O) dissolved in 53.8 ml H₂O. The resultant mixture had the following composition: 0.382 mole SiO₂, 0.0131 mole Al₂O₃, 0.0159 mole Na₂O, 0.118 mole [(CH₃CH₂CH₂)₄N]₂O, 6.30 moles H₂O. The mixture was placed in a Pyrex-lined (Pyrex is a trade mark) autoclave and heated at 150°C for six days. The resultant solid product was cooled to room temperature, removed, filtered, washed with 1 liter H₂O and dried at 230°F. A portion of this product was subjected to X-ray analysis and identified as ZSM-5. A portion of the product was calcined at 1000°F in air for 16 hours and the following analyses were obtained:

TABLE 5

Wt. % SiO ₂	93.62	Wt. % n-Hexane adsorbed	10.87
Wt. % Al ₂ O ₃	4.9	Wt. % Cyclohexane adsorbed	3.60
Wt. % Na ₂ O	1.48	Wt. % H ₂ O adsorbed	9.15
Total	100.00		
SiO ₂ /Al ₂ O ₃	32.5		
Na ₂ O/Al ₂ O ₃	0.5		

EXAMPLE 2

- A sample of a zeolite identified as ZSM-5 prepared in a manner analogous to that set forth in Example 1 was calcined at 1000°F in air for 16 hours then evaluated for its ability to crack an Amal Gas Oil. The Amal Gas Oil employed was a 650-850°F boiling range waxy Amal Gas Oil containing 25.2 weight percent normal paraffins ranging from C₁₁'s to C₃₄'s.

- The Amal Gas Oil was contacted with the ZSM-5 at 107 WHSV, 0.56 Cat/Oil ratio and 900°F ("Cat/Oil ratio" is an expression of catalyst effectiveness applied to any single run: it is the ratio of weight of catalyst employed to weight of feedstock processed). Analysis indicated that the waxy normal paraffin content of the Amal Gas Oil had been reduced from 25.2 weight percent to 4.1 weight percent, i.e., over 90% of the normal paraffins present in the charge were cracked to lower boiling products.

EXAMPLE 3

- The procedure of Example 2 was repeated with the exception that a commercially available zeolite, i.e., zeolite A, which had been base exchanged with a lanthanum salt was used in place of the ZSM-5. Even when more drastic operating conditions were employed, i.e., the space velocity was reduced to 6 WHSV and the Cat/Oil ratio raised to 1, the normal paraffin content could only be reduced to 16.5 weight percent.

- Thus, a comparison of the results of Examples 2 and 3 shows that the novel process of this invention permits a greater reduction in high molecular weight waxy normal paraffins to a degree which had previously not been

possible due to the fact that these long-chained molecules have a tendency to clog the pores of the heretofore available shape selective molecular sieves, thereby presenting problems in diffusivity which leads to less than favorable results.

EXAMPLE 4

This example will illustrate the improved results which can be obtained by the hydrocarbon processing of the present invention due to the fact that the catalysts employed are able to not only convert normal paraffins, but also slightly branched-chain paraffins—which are also detrimental to product value.

The same waxy Amal Gas Oil used in Example 2 was subjected to conventional extraction techniques utilizing a 5A zeolite. This extraction was continued until substantially all the normal paraffins from the Amal Gas Oil were removed. This is not a catalytic process, but merely a conventional extraction process. The Amal Gas Oil had a pour point of 100°F and after removal of all the normal paraffins, its pour point was lowered to 40°F.

Another portion of the same waxy Amal Gas Oil was subjected to shape selective cracking with a ZSM-5 catalyst prepared in the manner analogous to that set forth in Example 1. The process was carried out at a temperature of 900°F for 10 minutes at a space velocity of 107 WHSV and a Cat/Oil ratio of 0.56. This resulted in recovery of a 650+ fraction having a pour point of -5°F with 3.6 weight percent of the normal paraffins still remaining.

Thus, it can be seen that although the lowering of pour point is dependent on the removal of normal paraffins, such is not the complete

answer in pour point lowering. The process of this invention permits the drastic lowering of pour point even though all the normal paraffins have not been removed. The catalysts employed in this invention also convert slightly branched paraffins which also have a detrimental effect on pour point.

EXAMPLE 5

A ZSM-5 zeolite was prepared in accordance to the general technique set forth in Example 1; it was then contacted with a saturated solution of ammonium chloride in order to replace the original cations associated therewith

and thereafter washed with water, dried and calcined in air at about 1000°F in order to convert it to the hydrogen form, i.e., H-ZSM-5.

A similar treatment with an ammonium salt was carried out on a natural crystalline aluminosilicate identified as erionite and then these two materials were evaluated for their ability to selectively crack normal hexane from a mixture of normal hexane 2,3-dimethylbutane and benzene at a 15:1 H₂/HC ratio, a pressure of 200 psi and a temperature of 700°F. These materials were evaluated for an onstream time of 15 minutes and three hours. The results were as follows:

Catalysts	Conversion, wt. %	
	15 minutes	3 hours
H-erionite	93.8	33.7
H-ZSM-5	97.9	97.8

The above table clearly and dramatically illustrates the truly remarkable and surprising results obtained utilizing H-ZSM-5. Thus, at 15 minutes the conversion between the hydrogen erionite and H-ZSM-5 was substantially the same. This is not too surprising since both these materials are very active cracking catalysts. However, the results obtained after three hours are totally unexpected in that the H-ZSM-5 material did not age, i.e., lose activity, as is generally the case with all other zeolites. As can be seen, the conversion with erionite dropped to 33.7% thereby showing a definite aging whereas the conversion with H-ZSM-5 was substantially unchanged

after three hours thereby illustrating the fact that the catalyst does not age.

EXAMPLE 6

In order to demonstrate the difference in the type of shape selectivity obtained utilizing the catalysts of this invention as opposed to the shape selective materials of the prior art, the same waxy Amal Gas Oil employed in Example 2 was subjected to shape selective cracking with a calcined sample of ZSM-5 prepared with a crystalline aluminosilicate identified as calcium A, i.e., Linde (trade mark) 5A. A comparison of the products obtained from cracking the same material are shown in the Table below.

	ZSM-5 52.4 wt. % conversion	Calcium A 8.2 wt. % conversion	Δ 5A
C ₁	0.8	1.2	-0.4
C ₂	6.3	11.0	-4.7
C ₃	27.1	20.8	+6.3
C ₄	27.5	30.5	-3.0
C ₅ — C ₁₂ (C ₅ — 400°F)	37.3	19.5	17.8
C ₁₃ — C ₁₆ (400—600°F)	nil	nil	—
Coke	1.0	17.0	-16.0

It is immediately obvious that the coke yield obtained by the novel process of this invention is dramatically lower than that obtained with a classic shape selective materials of the prior art. In addition the gasoline make, i.e., the C_5-C_{12} is considerably higher than that with the Calcium A-type materials. Additionally, the classic shape selective catalyst of the prior art always yields products which are rich in C_3 hydrocarbons and conversely poorer in C_5-C_{12} hydrocarbons. As can be seen, such is not the case utilizing the ZSM-5 type catalysts, thereby indicating that not only normal paraffins, but slightly branched-chain paraffins are also converted. The enhanced results are believed demonstrated by the above table.

The following examples will indicate that it is also possible to obtain improved results utilizing hydrogenation/dehydrogenation components in association with the ZSM-5 type catalysts.

EXAMPLE 7

A ZSM-5 type catalyst was prepared following the general procedure of Example 1. The reaction composition and characteristics of the finished product are as follows:

TABLE 6

Temp., °C	150
Time, Days	5
Reaction Composition	
SiO ₂ /Al ₂ O ₃	29.1
Na ₂ O/Al ₂ O ₃	1.19
TPA ₂ O/Al ₂ O ₃	9
H ₂ O/TPA ₂ O + Na ₂ O	47
Composition	
Na ₂ O, Wt. %	2.42
Na, Wt. %	1.8

Al ₂ O ₃ , Wt. %	6.1	
SiO ₂ , Wt. %	90.6	40
Total	100.12	
SiO ₂ /Al ₂ O ₃	25.2	
Na ₂ O/Al ₂ O ₃	0.65	
Adsorption—Cyclohexane, Wt. %	3.07	
Normal Hexane, Wt. %	9.88	45
H ₂ O, Wt. %	7.51	

The above material was then calcined at about 1000°F for 16 hours and divided into two portions. Portion A was exchanged with 100 ml of a 0.5N aqueous solution of ammonium chloride at room temperature for one hour to form the ammonium salt. This was labeled Catalyst A1. Three grams of Catalyst A1 was exchanged with 35 ml of a 0.5N 2.9/1 zinc/NH₄ chloride solution at 109°F for four hours. The material was then washed with water and dried in air to yield a catalyst having a zinc content of 0.9 weight percent and a sodium content of 0.2 weight percent. This catalyst was labeled A2.

Portion B was treated with anhydrous ammonia (100 cc per minute) at room temperature to reconstitute the NH₄ sites. This catalyst was labeled B1. Three grams of Catalyst B1 was exchanged with a 0.5N solution of zinc and ammonium chloride as above. The finished catalyst contained 1.2 weight percent zinc and 0.3 weight percent sodium and was labeled B2.

EXAMPLE 8

Catalyst B2 supra, was then evaluated for pour point reduction of shale oil by hydroprocessing techniques. The charge stock was a full range dehydrated shale oil having a pour point of about +80°F. A typical composition is shown in the following table.

	Fraction, % *							
	0—10	10—20	20—30	30—40	40—50	0—50	50—100	0—100
Nonhydrocarbons, Wt. %								
N compounds	12	14	21	26	33	21	51	36
S compounds	5	4	4	5	5	5	7	6
O compounds	12	17	18	17	16	16	22	19
	29	35	43	48	54	42	80	61
Hydrocarbons, Wt. %								
n-Paraffins	8	8	8	8	10	8	3	6
Isoparaffins + naphthenes	7	6	4	3	3	5	5	5
n-Olefins	10	9	11	11	9	10	3	6
Iso-olefins + cyclo-olefins	31	25	19	14	12	20	5	12
Monocyclic aromatics	6	8	6	6	5	6	2	4
Polycyclic aromatics	9	9	9	10	7	9	2	6
Total	71	65	57	52	46	58	20	39

* A partial separation by molecular weight effected by distillation. The shale oil was distilled into 5 successive 10% fractions and a 50% residue. The figures 0—10 etc. represent the fraction in question, e.g. 10—20 represents the second 10% fraction.

5 The above shale oil was contacted with Catalyst B2 at 500 psig, 4 LHSV, 800°F. and 2,000 SCS/BBL hydrogen circulation. The results obtained showed a 97 weight percent recovery having a pour point of -15°F . An analysis of the liquid product having a -15°F pour point showed that there was olefin saturation and a shift to lower boiling products resulting in increased naphtha and light fuel oil content with a corresponding decrease in the greater than C_{22} range products, as shown by the following table. 10

	Charge	C_5 + liquid product
C_5 + naphtha	10.0	15.4
Light fuel oil	16.9	18.2
Higher products	73.1	66.4

15

EXAMPLE 9

This example will illustrate the manufacture of lube oil by shape selective hydrodewaxing.

The lube oil charge stock employed had the following properties:

Gravity, °API	31.9	20
Pour Point, °F	+85	
Sulfur, Wt. %	0.17	
Hydrogen, Wt. %	13.23	
K.V. @ 100°F, cs	19.27	

	K.V. @ 210°F, cs	3.93	90%	834	10
	Viscosity Index	108.4	95%	847	
	Vacuum Assay, °F		The above charge stock was subjected to hydrodewaxing with a zinc/H—ZSM—5 catalyst prepared in the manner set forth in Example 7 (B2), the experimental results as well as the various operating conditions are set forth in the table below.		
5	IBP	669			
	5%	696			
	10%	707			
	30%	737			15
	50%	766			
	70%	795			

Temperature, °F	700	700	650	650	C
LHSV	4	16	16	24	H
Pressure, psig	500	500	500	500	A
H/HC Mole Ratio	38	38	38	38	R
Conv., Wt. %	33	30.5	25.0	20.5	G
Hydrodewaxed Lube					E
Yield, Wt. %	67	69.5	75.0	79.5	100
Pour Point, °F	-40	-20	+25	+40	+85
K.V. @ 100°F	31.18	29.55	22.18	—	19.27
K.V. @ 210°F	4.85	4.75	4.15	—	3.93
Viscosity Index	76.9	81.0	95.7	—	108.4

From the above table, it can be seen that the instant catalyst resulted in a substantial lowering of a pour point from an original value of +85° to as low as -40°F.

The above results suggest that the catalytic processing of this invention can be employed in those areas where is desirable to hydrodewax charge stocks in order to obtain products of enhanced value. One such area would be in the preparation of automatic transmission fluids. The above process can replace the conventional solvent dewaxing presently employed. As another alternative, it is visualized that a particular charge stock can be subjected to conventional solvent dewaxing in order to reduce the pour point to some intermediate level and then this product subjected to shape selective hydrodewaxing in order to further lower the pour point. As can be seen, the processing techniques of this invention give greater flexibility to the refiner in the manufacture of commercially significant products.

EXAMPLE 10

This example will illustrate the shape selective hydrodewaxing of lube oil stocks and will again illustrate that hydrocracking of long chain molecules can be achieved.

The charge stock employed was a mid-continent vacuum tower overhead fraction having the following specifications.

Gravity, °API	32.2	
Gravity, Specific	0.8644	50
Vacuum Assay, °F		
IBP	550	
5%	596	
10%	630	
30%	646	55
50%	662	
70%	684	
90%	728	
95%	756	
Pour Point, °F (D-97)	+50	60
Flash Point, °F	345	
Viscosity, SUS, 100°F	57.7	
SUS, 130°F	45.8	
SUS, 210°F	34.5	
Kinematic, 100°F	10.56	65
Kinematic, 210°F	2.50	
Viscosity Index	56	
Aniline No., °F	182.2	

This charge stock was contacted with a Zn/H—ZSM—5 catalyst prepared in accordance with the techniques set forth in Example

7 (B2). The operating conditions were generally mild hydrocracking conditions, i.e., 500 psi, 700°F, 4 LHSV and a hydrogen to hydrocarbon mol ratio of 30. The results obtained are shown in the following table.

5	Run time (hrs.)	2
	Conversion, Wt. %	33.5
	Yields, Wt. %	
	C ₁ + C ₂	1.4
10	C ₃	5.4
	C ₄	10.1
	C ₅ + cracked product	16.6
	Unconverted	66.5
15	Pour Point, °F of unconverted product	-85°

As can be seen from the above data, the process of this invention resulted in a substantial lowering of the pour point of the product, i.e., from +50° to -85° or a 4.5°F lowering per percent conversion. Yield was 70 weight percent of the 600°F plus liquid product. This example clearly indicates the improved results which are obtainable by the novel processing

techniques of this invention.

EXAMPLE 11

This example will illustrate the preparation of a low freezing point high BTU jet fuel prepared by the novel process of this invention.

A 350—500°F Amal-Nafoora kerosene having the following properties:

Gravity, °API	48.1
Freeze Point, °F	-27
Aromatics (LIA) Vol. %	9.1
Aniline No., °F	156.9
Heating Value, BTU/lb.	18,710

This charge stock was contacted with a Zn/H—ZSM—5 catalyst prepared in accordance with the techniques set forth in Example 7(B2). The operating conditions were 500 psig, 650°F, 24 LHSV, 15/1 mole ratio H₂/HC. The above procedure resulted in obtaining a 78.5% yield of a dewaxed product whose properties, together with those of a JP—7 jet fuel, will be shown in the following table:

Gravity, °API	47.2	44—50
Freeze Point, °F	-63	-50
Aromatics (FIA) Vol. %	11.9	5
Aniline No., °F	148.9	—
Heating Value, BTU/lb.	18,655	18,750

The results shown in the above table illustrate the fact that the novel process of this invention is capable of significantly lowering the freeze point of an Amal kerosene. It is noted, however, that the heating value and aromatic content of the product fall outside the specification for JP—7 jet fuel.

In order to raise the heating value and lower the aromatic content, the hydrodewaxed product can be subjected to a mild hydrogenation treatment. In this connection 20 grams of the hydrodewaxed product, 100 ml of cyclohexane, 11 grams of a commercial catalyst comprising reduced nickel on Kieselguhr (Harshaw (trade mark) Ni 0107) were charged to a 300 ml stirring autoclave and 500 psig hydrogen was added. The above mixture was heated at 587—600°F is about 2 hours at which time the final pressure was about 1200—1300 psig. The above procedure resulted in a 93 wt. % recovery of a hydrogenated product which had the following products:

70	Gravity, °API	47.5
	Freeze Point, °F	-81

Aromatics (FIA) Vol. %	4.0
Aniline No., °F	179.0
Heating Value, BTU/lb.	18,835

From the above, it can be seen that the process of this invention provides a method of producing jet fuels having a low freeze point and a high BTU content.

WHAT WE CLAIM IS:—

1. A dewaxing process for the selective cracking of straight-chain hydrocarbons and slightly branched-chain hydrocarbons from a mixture of the same with compounds of different molecular shapes which comprises contacting said mixture with a crystalline zeolitic material having pore openings which are of a generally elliptical shape wherein the major axis of said ellipse has an effective size under conversion conditions of from about 5 to about 9 Å units and the minor axis about 5 Å so that said straight-chain and slightly branched-chain hydrocarbons are capable of entering into the internal pore structure of the zeolite and being converted.

2. The process of claim 1 wherein said zeolitic material is crystalline aluminosilicate.
3. The process of claim 1 or claim 2 wherein said zeolitic material has a hydrogenation/dehydrogenation function.
4. The process of any of claims 1 to 3 wherein said slightly branched hydrocarbon does not possess a quaternary carbon atom.
5. The process of any preceding claim wherein said mixture contains cyclic compounds.
6. The process of any of claims 2 to 5 wherein said crystalline aluminosilicate has an X-ray diffraction pattern substantially as set forth hereinbefore in Table 1.
7. The process according to any preceding claim which comprises contacting said mixture with the zeolite termed ZSM—5 herein under cracking conditions such that the straight-chain hydrocarbons and slightly branched hydrocarbons are able to enter into the pores of the ZSM—5 and be cracked.
8. The process according to any of claims 1 to 6 which comprises contacting said mixture with the zeolite termed ZSM—8 herein under conversion conditions such that the straight-chain hydrocarbons and slightly branched hydrocarbons are able to enter into the pores of the ZSM—8 and be cracked.
9. The process of any preceding claim wherein the dewaxing is carried out in the presence of added hydrogen.
10. The process of any preceding claim wherein said mixture is petroleum charge stock having an initial boiling point above 350°F.
11. A dewaxing process for the selective cracking of straight-chain hydrocarbons and slightly branched-chain hydrocarbons from a mixture of the same with compounds of different molecular shapes, which comprises contacting said mixture with a crystalline zeolitic material having pore openings which are of a generally elliptical shape, substantially as herein described in any of Examples 2, 4 to 6 and 8 to 11.
12. Dewaxed petroleum charge stocks whenever produced by the process claimed in any of claims 1 to 11.
- For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24 Southampton Buildings,
Chancery Lane,
London, W.C.2.